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# Technical Report

## ANODES FOR PREPARATION OF ALKALI PERCHLORATES

For: Office of Naval Research  
Washington 25, D. C.

By: Horizons Incorporated  
Cleveland, Ohio  
This document has been reviewed in accordance with  
OPNAV 115-1, 115-2, 115-3, 115-4, 115-5. The security  
classification and reason is correct.

Date: 9/16/53

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Chief of Naval Research (Code 25)

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Submitted To:

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I. SUMMARY

The objective of the present research is to find a material to replace platinum as anode in the industrial preparation of sodium perchlorate from sodium chlorate by electrolysis. Classes of material considered to be particularly promising for investigation include: (1) silicides such as those of molybdenum and titanium, and (2) modified magnetites such as those embodying titanium oxide and copper oxide in their structure. The investigation includes, but is not restricted to, such materials.

A unit was constructed and is operational which permits small scale testing of four anodes at a time under conditions similar to those prevailing in the industrial process. Of the magnetite-class materials, pellets were prepared of varying composition and under several firing conditions in a search for bodies of lowest resistivity. Some preliminary experiments were performed on magnetite anodes and on silicide-class anodes. Process tests were run on specimens of (a) 70% dense chromium, (b) 77% dense chromium, (c) tungsten carbide, (d) Smith alloy, (e) tantalum, (f) nimonic alloy, (g) inconel alloy, (h) titanium carbide, and (i) TiO.

The effect of superimposition of alternating current on the direct current circuit including the sodium chlorate electrolyte was investigated.

A series of experiments using surface treated steels as perchlorate anodes was carried through.

Theoretical considerations relevant to the perchlorate anode problem were explored.

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II. PROCESS TEST EQUIPMENT AND PROCEDURE

In planning the cells and procedure for small scale tests of perchlorate anode materials it was desired to duplicate the most important parameters in actual production practice as closely as possible. The Penn Salt literature review<sup>(2)</sup>(p. 25) outlined operating conditions prevalent at Western Electrochemical Co., Cardox Corp., and I. G. Farben. A-G plants. This information constituted our guide in the matter.

It was reported<sup>(2)</sup> that present commercial practice involves cooling the operating cells so that the operating temperature is about 50°C. On our scale of operations we found it necessary to provide heat in order to maintain this temperature. A thermostat which could be maintained at  $50 \pm 0.5^\circ\text{C}$  was converted to a test unit with positions for four large test tubes (4.5 cm. i. d. x 19 cm.) as cells. Cathodes consisted of 24 gauge mild steel strips (Cleveland Steel Products) 4.2 cm. high x 12.5 cm. long, rounded to fit into the cells. An extension strip, 6 cm. x 15 cm, of-a-piece with the main body of the cathode, extended up and out of the cell and served as an electrical lead. The latter was coated with silicone grease to minimize corrosion by bath vapors.

Each cell was fitted with a rubber stopper with a hole at the center through which extended a piece of glass tubing almost reaching to the electrolyte level. The test anode with platinum wire lead-in was supported in this tube. Off-center in the rubber stopper was another hole fitted with a length of glass tubing. This served as a support and bearing for a stirring rod. Stirring rods in all four cells could be motor driven simultaneously by use of a drive belt. However, recent experiments suggest that auxiliary stirring might be a needless complication as

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cathodic hydrogen evolution appears to provide excellent agitation.

Power was provided by storage batteries. Each cell was equipped with an Ammeter and Voltmeter to indicate current through and voltage across the electrodes.

Electrolyte charged to a cell consisted of 100 cc of sodium chlorate solution (600 g/l.) and 10 cc of sodium dichromate dihydrate solution (40 g/l.).

The current density selected as norm was 300 milliamps/sq. cm. However, due to the great variation in shapes, sizes and resistances of the various materials tested in the early work, current densities have deviated widely from this norm. As tests become more routine and involve evaluation of four similar anodes at one time it is planned to realize the normal current density.

Failure of test anodes was found to occur in two ways: (1) Conductivity fell sharply in the first minutes of electrolysis until negligible current flowed. This behavior is denoted "polarization" for the present purposes, or (2) The anode suffered serious attack during the electrolysis resulting in dispersion of its substance through the bath. This behavior is described as "disintegration". When anodes failed in either of these ways, the description of their behavior comprised the main outcome of the "process-test".

With anodes which suffered minor attack, electrolysis was ordinarily carried to an extent where, on the basis of 100% current efficiency, the sodium chlorate content was calculated to be about 10 g/l. The bath solution was then filtered with washing into a 1000 cc volumetric flask and diluted to the mark. Analysis for chloride and chlorate were performed on portions of this solution. Total sodium chloride and sodium



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chlorate amounts were calculated. The sodium-perchlorate produced was computed by difference.

Other data taken for anodes included: (1) mass, (2) dimensions, (3) electrical resistance, (4) extent anode immersed in electrolyte. Computed parameters included: (1) anode density, (2) current density, (3) current yield of perchlorate.

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III. MAGNETITE-CLASS ANODES

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To serve as an electrode a body must have reasonably low electrical resistance. Too high resistance would result in an unacceptable power requirement for the process. In addition, the  $I^2R$  heating might contribute to deterioration of the electrode material and excessive heating of the electrolytic bath. Our initial problem in magnetite-base bodies has been to attain good electrical conductivity. Magnetite itself is one of the best electrical conductors among the minerals.<sup>(1)</sup> Its resistivity is said to be about 850 times that of mercury ( $850 \times 95.8 \times 10^{-6} = 0.08$  ohm-cm). It is desirable that this resistivity be diminished for our purpose, and to this end we have prepared pellets of modified magnetite over a range of compositions and under several conditions of firing and determined the electrical resistance of the resulting bodies. Our plan is to make up the best materials in the form of rods and submit them to process testing.

Several years ago Horizons developed a magnetite composition which could be fired to complete vitrification of such nature that a polish of mirror finish could be applied to the surface on a production basis. These compositions consisted substantially of iron oxide with minor percentages of copper oxide and titanium oxide. The ranges of composition were as follows:

Copper oxide	2 to 10%
Titanium oxide	8 to 40%
Iron oxide	Balance

Such compositions were expected to vitrify in a temperature range  $1060^\circ\text{C}$  to  $1200^\circ\text{C}$ . The higher the copper oxide content, the lower the temperature of vitrification.

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For the first experiments ten compositions were selected in these series. These are indicated in Table 1. The purpose of this set of experiments was to determine the effect on the conductivity of each of the three components and thus enable limitation of the field of suitable compositions.

#### Experimental Procedure for Preparing Magnetite Pellets

The following materials were selected as ingredients:

1. Ferric oxide, 99.2%  $\text{Fe}_2\text{O}_3$ , C. K. Williams, Lot 1599
2. Cupric oxide,  $\text{CuO}$ , Mallinckrodt, Analytical Reagent
3. Titanic oxide,  $\text{TiO}_2$ , Titanium Pigment Corp., 99.5% pure

The ingredients were weighed out and hand mixed in a mortar and pestle until complete blending was achieved. The bodies were then calcined in air for one hour at 925-1025°C. The resulting calcines were ground to pass a 200 mesh sieve.

Sample pellets 0.5" diameter x 0.2" thick were pressed in a two plunger die at a pressure of 5 tsi. No binder was used in the pressing operation. Ten samples of each composition were prepared. The pellets were placed on alumina trays for firing.

#### Firing Procedure and Results

The pellets were fired in the selected atmosphere for 1 hour at 1090-1200°C. Resistance was measured on each pellet with a Simpson Ohm Meter (Simpson Electric Co., Chicago, Illinois, Model 260) for the higher resistances and on a Wheatstone Bridge (Rubicon Co., Philadelphia, Cat. 1052) for the lower values. Resistivities were computed by means of the usual equation

$$\rho = R \frac{A}{L}$$

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TABLE 1(1) Resistivity of Magnetite Compositions

RESISTIVITY

Product Number	Percentage Composition			Air Firing			Nitrogen Firing			Argon Firing			Argon (80)-	Argon (96.7)-
	Fe <sub>2</sub> O <sub>3</sub>	CuO	TiO <sub>2</sub>	A	B	C	A	B	C	A	B	C	Hydrogen (20) (ohm-cm x 10 <sup>3</sup> )	Hydrogen (3.3) (ohm-cm x 10 <sup>3</sup> )
96-1	90	C	10	1.3	1.9	0.6	0.9	0.4	0.9	14	15	14	43	—
96-2	90	2	8	3.3	3.8	2.8	0.5	0.9	0.6	9	10	9.5	41	43
96-3	90	5	5	7.0	4.9	4.9	0.6	0.5	1.2	12	11.5	11	19	51
96-4	85	5	10	5.7	3.9	6.9	0.9	1.7	2.2	13	15	13	18	79
96-5	80	15	5	9.5	7.9	10.0	149.0	69.3	70.6	77	84	79	—	—
96-6	80	10	10	3.4	4.7	1.7	109.7	99.4	117.1	57	42	49	—	—
96-7	80	5	15	4.5	5.7	3.8	2.4	1.9	2.4	17	23	17	19	62
96-8	65	30	5	27.8	24.8	20.9	17.5	13.3	13.7	1,010	919	868	—	—
96-9	65	17.5	17.5	37.3	23.4	20.8	6.4	6.5	6.8	483	483	479	—	—
96-10	65	5	30	42.1	32.3	43.6	7.0	8.4	11.9	334	291	257	26	9300

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(1) Laboratory Notebook Reference 151, pp. 8-17

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where  $\rho$  is the resistivity, R the resistance, A the area of the pellet, and l the thickness of the pellet.

Direct results of this set of experiments are presented in Table 1. The firing atmosphere is indicated in each case. For the air firing and nitrogen firing resistivities are in thousands of ohm-cm; for the argon firings, in ohm-cm; for the firings involving hydrogen, in thousandths of ohm-cm.

Since the measured resistivities varied by a factor of  $10^5$  it was thought desirable to present the data in somewhat different form for ready interpretation. Table 2 comprises values of logarithms of resistivities (in milli ohm-cm.) for the several compositions and firing conditions. For comparison purposes it is to be noted that the logarithm of the milli ohm-cm. resistivity of unmodified magnetite is about 1.90 based on 0.08 ohm-cm. for the resistivity.

Examination of Table 2 shows that resistivities of this order were approached only in the case of atmospheres containing hydrogen. Reduction to uncombined metal was suspected and a metallographic analysis of a sample prepared in the argon-hydrogen (80-20) atmosphere indicated that such might be the case. The product of reduction by hydrogen is water vapor. If we write the equation:



we can formulate the first approximation to the equilibrium constant K as

$$K = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$$

and can take the reducing ability to be proportional to  $1/K$  or  $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ . Thus, it is possible to "tailor" an atmosphere containing water vapor and hydrogen in respect to reducing power by controlling the proportion of these two components.

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TABLE 2

Log Resistivity of Magnetite Compositions

Product Number	Percentage Composition			Log Resistivity (log milH ohm-cm)				
	Fe <sub>2</sub> O <sub>3</sub>	CuO	TiO <sub>2</sub>	Air	Nitrogen	Argon	Argon (80)- Hydrogen (20)	Argon (96.7) Hydrogen (3.3)
96-1	90	0	10	6.11	5.87	4.16	1.63	—
96-2	90	2	8	6.52	5.83	3.98	1.61	1.63
96-3	90	5	5	6.75	5.87	4.06	1.28	1.71
96-4	85	5	10	6.74	6.21	4.15	1.26	1.90
96-5	80	15	5	6.96	7.98	4.90	—	—
96-6	80	10	10	6.52	8.04	4.69	—	—
96-7	80	5	15	6.67	6.34	4.28	1.28	1.79
96-8	65	30	5	7.39	7.17	5.97	—	—
96-9	65	17.5	17.5	7.44	6.82	5.68	—	—
96-10	65	5	30	7.59	6.96	5.47	1.42	3.97

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H<sub>2</sub>O (vapor) - H<sub>2</sub> Mixtures in N<sub>2</sub> Carrier

Prompted by the above considerations a set of four preliminary experiments was carried through using a firing atmosphere of the following compositions:

H<sub>2</sub>O - 81.85%

H<sub>2</sub> - 0.8%

N<sub>2</sub> - 17.35%

For comparison purposes, pellets of composition 96-5, 96-6, 96-8, and 96-9 were used in these tests. The results are presented in Table 3.

A reasonable interpretation of the data in the table is obtained if we postulate that the resulting resistivity varies directly as the proportion of TiO<sub>2</sub> and inversely as the proportion of CuO. Compositions 96-5, 96-6 and 96-8 exhibit this relation in a straightforward manner. With composition 96-9 to apply the interpretation we must assume that the large proportion of TiO<sub>2</sub> overrides the CuO effect resulting in a net increase in resistivity.

It was considered that, with some of the bodies tested, elemental copper might have formed and contributed to the enhanced conductivity. Product 96-8 of Table 3 was submitted to an X-ray examination and the presence of free copper was confirmed. We cannot predict the effect of the presence of copper on the behavior of the body as a perchlorate anode. For example, it may be that a proper protective film will form which will render such copper in the substrate immune to the attack.

Further Variation of Firing Atmosphere

Further experiments were performed with the object of determining the optimum firing atmosphere. Pellets were made of certain of the earlier compositions and also of some new compositions. Results are

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TABLE 3(1)

Electrical Resistances of Bodies Produced in

$H_2O-H_2-N_2$  (81.8%-0.8%-17.4%)

Firing Atmospheres

<u>Product Number</u>	<u>Percentage Composition</u>			<u>Resistivity (milli ohm-cm)</u>	<u>Log Resistivity<sup>(2)</sup> (log milli ohm-cm)</u>
	<u>Fe<sub>2</sub>O<sub>3</sub></u>	<u>CuO</u>	<u>TiO<sub>2</sub></u>		
96-5	80	15	5	102	2.01
96-6	50	10	10	679	2.83
96-8	65	30	5	21	1.33 <sup>(3)</sup>
96-9	65	17.5	17.5	1520	3.18

- (1) Laboratory Notebook Reference: 151, 20-21
- (2) Log resistivity of a natural magnetite: 1.90
- (3) X-ray examination indicated substantial elemental copper present in this sample.

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TABLE 4(1)

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Resistivity as a Function of Firing Atmospheres

Product Number	Percentage Composition			Resistivity (Ohm-cm)		
	Fe <sub>2</sub> O <sub>3</sub>	CuO	TiO <sub>2</sub>	H <sub>2</sub> O(v.) <sup>(2)</sup>	H <sub>2</sub> O(v.)-H <sub>2</sub> - N <sub>2</sub> (82-.8-17) <sup>(3)</sup>	H <sub>2</sub> O-H <sub>2</sub> (97.4-2.6) <sup>(4)</sup>
96-1	90	0	10	534	29.4	179
96-2	90	2	8	108	8.8	0.86
96-3	90	5	5	66	---	0.12
96-4	85	5	10	58	5.9	1.9
96-5	80	15	5	---	---	0.18
96-6	80	10	10	---	---	1.86
96-7	80	5	15	56	6.6	10.6
96-8	65	30	5	---	---	0.038
96-9	65	17.5	17.5	---	---	14.7
96-10	65	5	30	---	---	495
96-11	95	2.5	2.5	126	7.3	0.037
96-12	90	10	0	70	4.5	0.050
96-13	85	0	15	154	33.3	101.9
96-14	85	2.5	12.5	77	8.8	7.6
96-15	87.5	2.5	10	71	17.2	1.3

(1) Notebook Reference: 151, 22-25

(2) Firing 1 hr. at 1150°C

(3) Firing 1 hr. at 1090°C

(4) Firing 1 hr. at 1150°C

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embodied in Table 4.

The expected effect of mixed hydrogen-water vapor as compared to the effect of water vapor alone is shown in a comparison of columns 5 and 6 in the table. Without exception the resistivity of all the bodies tested was lower with the hydrogen atmosphere. Column 7 of Table 4 embodies the results of firings done in the absence of the nitrogen carrier with a  $H_2$ - $H_2O$  mixture somewhat richer, in proportion, in hydrogen. It is seen that lower resistivities were achieved except with the compositions containing no  $CuO$  (96-1 and 96-13). Composition 96-7 is not regarded as a serious exception to this statement. Three of the products (96-8, 96-11, and 96-12) show lower resistivities than unmodified magnetite (0.080). Since the atmosphere of column 7 is inherently more reducing by virtue of the  $H_2$ - $H_2O$  ratio than the atmosphere of column 6 we cannot tell whether the absence of nitrogen also contributed. It would be of some interest to have data bearing on this question.

#### Bodies Selected for Process Testing

As a result of the several series of experiments reported above it was considered possible to make a reasonable selection of the bodies that offered most promise for use as perchlorate anodes. Rods approximately 1/2" diameter x 4-1/2" long are being fabricated and will be subjected to process testing shortly.

For firing in a 97% Argon-3% Hydrogen atmosphere the following compositions were selected.

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TABLE 5

Percentage Composition

<u>Product No.</u>	<u>Fe<sub>3</sub>O<sub>4</sub>%</u>	<u>CuO%</u>	<u>TiO<sub>2</sub>%</u>
96-1	90	0	10
96-2	90	2	8
96-3	90	5	5
96-4	85	5	10
96-7	80	5	15

For firing in a 0.8% H<sub>2</sub> - 82% H<sub>2</sub>O vapor - 17% N<sub>2</sub> atmosphere all compositions 96-1 through 96-15 in Table 4 will be tried.

Some Tests with Unmodified Magnetite

While the above sets of experiments with magnetite-copper oxide-titania ternaries were being carried through, it was considered desirable to make some preliminary tests with unmodified magnetite. A material supplied by Foote Mineral Company as Fe<sub>3</sub>O<sub>4</sub> was mixed with 1% methocel to serve as a binder and the mix extruded and fired in air.

From the descriptions below it will be noted that the action of magnetite relative to corrosion varies depending on whether the anode is wholly below the liquid level or not. It is suspected that most of the weight losses experienced occur above the electrolyte level. If the rod is completely vitreous this difficulty may be by-passed by using a ceramic or glass protective sleeve above the electrolyte level and extending to just below the surface.

Anode 123-31

This anode was a rod of the above material. It had a resistivity of about 8 ohm-cm., a million times the resistivity of platinum (10<sup>-8</sup> ohm-cm). The density was 4.3 g/cc., 83% of the theoretical density, 5.2 g/cc. Dimensions of the rod were 1 cm.diameter x 10.4 cm. long.

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The anode was immersed to a depth of 2 cm. in the electrolytic bath. A potential of about 6 volts across the cell was only able to drive a current of about 0.1 ampere through the system. The behavior of the anode at such a low current would have little significance even if we carried on electrolysis for some time. Therefore, the test was terminated after about 3-1/2 hours.

After observing the behavior of Anode 123-32 (see below) it occurred to us that 123-31 might also be made to behave more satisfactorily. Thus, 123-31 was worked to a smoother surface on a grinding wheel and a groove cut in the top to provide better contact with the platinum lead-in wire.

Immersion of this anode to a depth of ca 7 cm. permitted electrolysis of about 0.1 amps at 12 volts. When the level of bath solution was increased so that the anode was fully immersed it was possible to electrolyze at 1.0 amps x 11.7 volts. We may presume that some of the electrolysis occurred at the surface of the platinum lead-in wire.

In view of the value for the resistivity of a magnetite given before, 0.08 ohm-cm., it is obvious that the material used here, having a resistivity of 8 ohm-cm, was defective in some way. Either the physical state (imperfectly compacted and sintered powder) or the composition (altered by the treatment) or both were unfavorable. This serves to emphasize the necessity for careful selection and control of conditions of preparation and possible contaminating substances present. It was mentioned in the Research Proposal that there was some question of the identity of so-called magnetites used in the past as perchlorate anodes. An objective of our experimentation is to produce sintered bodies in which the conductive magnetite crystal structure is maintained.

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Anode 123-32

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A second rod of the same composition as 123-31 was polished on a grinding wheel and a groove cut around the top so that contact of the platinum lead-in wire was made to a lower layer of material. Dimensions of this anode were 1.15 cm. diameter x 5.09 cm. long. It weighed 19.35 g. initially and suffered a loss of about 0.13 g. during course of a 25.6 ampere-hour electrolysis. The current density was held at about 100 milliamps per square centimeter and current yield (based on a preliminary analysis) was essentially 100% of theoretical.

The electrolysis was performed with the anode completely immersed. This, of course, meant that part of the platinum lead-in wire dipped under the solution. The original smooth surface of the anode was roughened during electrolysis consistent with the loss in weight mentioned.

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#### IV. Silicide-Class Anodes

Our program calls for the investigation of refractory silicides such as those of molybdenum, titanium, and zirconium in use as anode materials for perchlorate production. The silicide selected for initial investigation was the molybdenum compound. As anticipated, the first problem was to develop the most appropriate method of fabricating powdered molybdenum disilicide into massive anode shapes of high density. With this work in progress preliminary tests were run on relatively porous rods of the material prepared by an extrusion-sintering technique.

The porosity of the  $\text{MoSi}_2$  may be a major factor in its disintegration. We have now developed techniques for producing  $\text{MoSi}_2$  rods of close to maximum density and these will be included in the program. Once these techniques are perfected various additives designed to improve the chemical performance of the material will be tried.

##### Anode 123-33

Molybdenum disilicide powder (-200 to -325 mesh) with methocel binder was extruded into rod form and sintered for 5 hours at  $1500^\circ\text{C}$  in hydrogen. Dimensions of this anode were 0.54 cm. diameter x 10.54 cm. long. The resistivity of the material was about 100 microhm-cm. ( $\text{MoSi}_2$  - 21.5) and the density 3.3 g/cc (theoretical 5.95).

The anode was immersed 6.8 cm. into the electrolyte. Electrolysis was started at a level of 2 amperes at 3.7 volts. It was possible to pass only about 0.5 amp.-hr. before the current fell to a low level (0.-0.4 amps.). The anode initially weighed 7.72 g. and suffered a loss in weight of 0.41 g. Towards the end of the electrolysis it was found that the platinum lead-in at the junction to the anode was coated

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with yellow crystals which apparently interfered somewhat with the flow of electricity through the contact. Fluctuation of the current between 0 and 0.4 amperes was observed. The anode itself was also coated with a yellow material. Aside from a few rust particles, presumably from the cathode, the bath was little changed in appearance by the electrolysis.

We may infer that electrolyte soaked into the anode by capillary action and rose to the top. Presumably, solution came out to the surface of the anode above the bath level and water evaporated leaving behind solid salt. It may be that when contact was made between electrolyte and the lead-in wire some anodic oxidation occurred directly on the platinum. These phenomena point up the necessity for using molybdenum disilicide anodes of the lowest possible porosity (highest density).

#### Anode 123-37

A mixture of molybdenum disilicide and silicon metal powders was prepared to a composition 98.1%  $\text{MoSi}_2$  and 1.92% Si and extruded into rod form. The rod was sintered for 24 hours at  $1300^\circ\text{C}$  in a hydrogen atmosphere. Dimensions of this anode were 0.5 cm. diameter x 14.5 cm. long. The resistivity of the material was about 60 microhm-cm. ( $\text{MoSi}_2$  - : 21.5) and the density about 3.94 g/cc. (theoretical: 5.95).

This anode was placed in a cell and a potential of about 6 volts applied. The initial current was about 6 amperes but fell within a minute to about 0.3 ampere. We may describe this general behavior by saying the anode "polarized". Doubling the voltage caused a momentary high value for current followed by an immediate fall. After 4-5 hours the current fell to a negligible value.

Inspection of the anode showed that electrolyte had reacted with it by

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capillary action, reached the lead-in wire at the top, and broke the contact by corroding the lead-in wire. The anode suffered no apparent attack; this cannot be regarded as significant because the current passed was small.

Anode 123-49a

Four 6" x 1/8" molybdenum disilicide rods were prepared by extrusion and placed in a 4" i.d. graphite crucible supported in a packing of high-purity alundum powder. The crucible and contents were heated in a vacuum induction furnace for about two hours. During this period the temperature rose from ambient to about 1500°C., and the sight glass was clouded rendering the later temperature readings only approximate. The initial pressure of 15 microns rose to about 230 microns.

After overnight cooling the crucible was examined and the rods found embedded in the alundum powder which had partially sintered around them. It was apparent that some volatilization of elemental silicon had occurred. It was possible to separate the rods from the matrix although not without breaking them into smaller lengths. Anode 123-49a was one of these shortened rods.

The anode was 0.63 cm. diameter x 5.94 cm. long. The density was 3.15 g/cc. compared with a theoretical of 5.95. The electrode was immersed in the bath to the extent of 4.9 cm. Electrolysis was begun at a level of 1.2 amps. x 4.0 volts and was carried on for 4.8 amp-hrs. to a level of 0.1 amps. x 6.8 volts. Initially the electrode weighed 5.84 g; it lost 1.60 g during the course of the electrolysis.

Consistent with the loss in weight reported, it was observed that the anode had largely disintegrated. Pieces of it were found in the bath.



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The section of anode above the bath level was not visibly attacked. The bath was quite cloudy and orange-yellow in color. It may be considered that the high porosity of the anode largely contributed to its failure to resist the oxidative attack.

Anode 123-49b

Anode dimensions were 0.64 cm. diameter x 7.24 cm. long. Density was 3.00 g/cc compared to a theoretical of 5.95 g/cc. The electrode dipped 4.7 cm. into the solution. Electrolysis was started at a level of 1.1 amps. x 5.2 volts and fell to 0.1 amp. x 10 volts after only 0.3 ampere-hours of electricity were passed. We may describe this behavior by saying that the anode "polarized"

The anode weighed 6.97 g. initially and gained 0.24 g. presumably due to soaking up electrolyte. A white coating had formed on its surface. The bath was colored orange apparently due to cathodic corrosion products (rust?). At the Pt and Cu junction on the anode lead-in some corrosion products were in evidence.

As described elsewhere, this anode was submitted to a test involving A. C. superimposition to see if its depolarization could be effected.

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V. Other Materials Tested as Anodes

In accordance with the main plan of research, the first materials selected for intensive investigation were the modified magnetites. As indicated elsewhere, the method of study used entailed a wide ranging variation of compositions and firing atmospheres on the pellet-scale and the testing of pellets for electrical conductance. This approach initially left the Process Test Unit available for use with other materials. Therefore, several promising materials were submitted to test.

Among materials tested were three alloys. Smith Alloy: Iron base with about 37.5% chromium, and 7.5% aluminum. Nimonic Alloy: Nickel base with about 16% chromium, 3-4% titanium, and 2% aluminum. Inconel alloy: Nickel base with about 13% chromium, 6% iron, and small amounts of manganese, silicon, and copper. These compositions should be taken as indicative rather than definitive for the particular specimens here reported.

123-41. 70% Dense Chromium

A rod of chromium of density 5.03 g/cc. (theoretical 7.20) 4.3 cm. long x 0.26 cm. diameter was immersed to a depth of 1.4 cm. in the electrolytic bath. Electrolysis was started at a level of 0.2 amps x 23 volts but fell within thirty minutes to zero amperes. The anode weighed 1.19 g. initially and increased in weight 0.05 g. during the course of the electrolysis. Absorption of solution into the chromium pores may have caused this increase in weight. Examination of the anode showed that it had lost its metallic luster and acquired a dull surface from the process. The bath solution had become slightly cloudy.

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123-47a. 77% Dense Chromium

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A rod of chromium of density 5.55 g./cc. (theoretical 7.20) 1.78 cm. long x 0.28 cm. diameter was immersed to a depth of 1.3 cm. in the electrolytic bath. Electrolysis was started at a level of 1.9 amps. x 14.5 volts and continued for 19.4 amp.-hrs. to a level of 1.45 amps. x 16 volts. The anode weighed 0.606 g. initially and decreased in weight 0.116 g. Attack occurred at the lead causing the electrode to finally fall into the solution. The bath attained an olive-green color and solid particles were suspended throughout. Analysis indicated that about two-thirds of the sodium chlorate was oxidized to perchlorate. About 0.5 g. sodium chloride was present in the final solution.

123-47b. 77% Dense Chromium

A rod of chromium of density 5.5 g./cc. (theoretical 7.20) of dimensions 1.93 cm. long x 0.28 cm. diameter was immersed to a depth of 1.3 cm. in the electrolytic bath. Electrolysis was started at a level of 3.4 amps. x 6.4 volts and after 3.64 amp.-hrs. fell to a level of 0.1 amp. x 11.5 volts. The initial weight of 0.652 g. was diminished by 0.140 g. during the course of the electrolysis. The electrolysis was discontinued when the electrode fell free of its platinum lead-in wire apparently due to a reduction in diameter by oxidative attack. Analysis indicated that the original 60 g. sodium chlorate had been diminished to about 57 g. and about 0.2 g. sodium chloride were present.

123-43. Tungsten Carbide

A rod of tungsten carbide of density 13.3 g./cc., 9.54 cm. long x 0.23 cm. diameter, was immersed to a depth of 4.4 cm. in the electrolytic bath. Electrolysis was started at a level of 4.2 amps. x 6 volts and after

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passage of 1.32 amp.-hrs. had fallen to 0.6 amps. x 20 volts. The electrode of initial weight 5.000 g. suffered a loss of 0.833 g. in the process. The final electrolytic solution was orange-green in color and contained a green sediment. The sodium chlorate content of the bath diminished only 1 g. and the sodium chloride content became 0.3 g.

#### 123-45. Smith Alloy

A bar of Smith Alloy of density 21.3 g./cc., 0.509 cm. x 0.510 cm. cross-section x 21.8 cm. long, was immersed to a depth of 7.4 cm. in the electrolytic bath. Electrolysis, began at a level of 5 amps. x 1 volt, fell to a level of 1.4 amps. x 16 volts after the passage of 12.7 amp.-hrs. of electricity. The anode of initial weight 29.36 g. suffered a loss of 9.90 g.; inspection showed the electrode suffered extremely serious corrosion. The bath was red-brown in color and viscous due to the large quantity of suspended solid.

#### 123-53. Tantalum Strip

A strip of ductile tantalum of dimensions 5.91 cm. x 0.62 cm. x 0.05 cm. was immersed to a depth of 4 cm. in the electrolytic bath. Electrolysis was started at a level of 0.8 amps. x 7.4 volts but fell immediately to 0 amps. x 8.9 volts, i. e., the anode polarized. The weight of the anode, 2.157 g., remained essentially unchanged.

Elsewhere, the behavior of this anode under superimposed A. C. is discussed.

#### 123-55. Nimonic Alloy

A piece of nimonic alloy, a material used for jet rotor blades, shaped in the form of a long pyramid (Base: 0.65 cm. x 0.5 cm. x 0.4 cm. Height:

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7.15 cm.) and immersed to a depth of 5 cm. in the bath was tested. Electrolysis was started at a level of 4.15 amps. x 4.8 volts and continued for 11.0 amp.-hrs. (4 hrs.) to a level of 0.8 amps. x 11.6 volts. The anode initially weighed 8.740 g. and lost 6.362 g.

Inspection showed that the anode was dissolved away up to the bath level. The anode and cathode had multi-colored coatings. The bath was viscous with a large quantity of suspended solid.

#### 145-197-1. Inconel Alloy

A bar of Inconel Alloy of dimensions 10.13 cm. x 0.75 cm. x 0.23 cm. was immersed to a depth of 7.83 cm. in the electrolytic bath. Electrical resistance of the bar was 3.5 milli-ohms. Electrolysis, begun at 2 amps. x 3.4 volts, fell to 0.1 amp. x 10.7 volts after 8.4 amp.-hr. (5.5 hours). The anode which initially weighed 13.00 g. lost 10.16 g. of material.

Inspection showed that the anode had dissolved away until it was no longer immersed in the solution. The surface of anode exposed by the oxidative attack exhibited a bright metallic luster. The bath was black with suspended particles. Gross pieces of material were found in the bath as well as some green sediment. The cathode was covered with a red coating.

#### 145-197-2. Titanium Carbide

A rod of titanium carbide which had been prepared by sintering at 2500°C of dimensions 4.23 cm. x 0.84 cm. diameter was completely immersed in the electrolytic bath. Resistance of the bar was 4.2 milli-ohms. Electrolysis began at 2 amps. x 4.4 volts and proceeded to 1 amp. x 8.2 volts with the passage of 14.1 amp.-hrs. of charge over a period of 10 hrs. 20 min. The anode which initially weighed 6.744 g. suffered a loss of 2.028 g.

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Examination showed the anode to be coated with a yellow substance and to be seriously disintegrated. A pungent odor was noted at the bath. The solution became yellow and foaming during electrolysis and black sediment was present in the bath. White particles also were present in large quantity.

145-197-3. TiO

A TiO rod which had been prepared by sintering at 2100°C of dimensions 13 cm. x 1.45 cm. diameter was immersed to a depth of 9 cm. in the electrolytic bath. The resistance of the rod was 18.8 milli-ohms. Electrolysis was started at a level of 2 amps. x 5 volts and carried to 0.5 amps x 10.7 volts for 6.8 amp.-hrs. (10 hours). Initial weight of the rod was 61.6 g.

The anode was coated with yellow and white crystals and a pungent odor was noted at the bath. Upon removal from the bath the anode broke in two. The bath, which had become milky during electrolysis, contained a large quantity of white precipitate.

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VI. A. C. Superimposed On D. C.

Experiments with 60 cycle A. C.

Scattered empirical information exists on the effects obtained when an alternating current is superimposed on an electrolytic direct current. However, the range of phenomena have not yet been well rationalized. While it was considered that higher frequencies might prove most fruitful, yet it was thought desirable to perform some experiments with line frequency (60 cycle) alternating current.

The method adopted of introducing A. C. into the electrolytic current was simple. The secondary coil of a filament condenser was connected in series with the D. C. line to the cell. The A.C. output of a line operated variable inductor (Variac) was fed to the primary coil of the filament condenser. Thus the D. C. was isolated from the A. C. source by the inductor and the A. C. was inductively coupled to the D. C. circuit. By this arrangement it was possible to superimpose an alternating current of the order of 1 ampere on the D. C. system.

Platinum Anode

An initial experiment with a platinum leaf anode (approximate dimensions 1.3 cm x 0.3 cm) was performed. It is to be noted that the D. C. ammeter and voltmeter in the electrolytic circuit did not directly respond to sixty cycle alternating current. The A. C. could affect the instruments only indirectly through changing the gross resistance of the circuit.

When the circuit was made operative it was immediately observed that the reading on the D. C. ammeter was greater the greater the A. C. input. The circuit did not provide a means of measuring the A. C. current while the

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D. C. was on, but as mentioned above, the former was of the order of 1 ampere. Table 6 below shows the variation of the apparent resistance R of the cell system for several levels of D. C. current with the A. C. on and off.

TABLE 6

Apparent Cell Resistance with Superimposed A. C.

<u>A. C. (1)</u>	<u>D. C. Volts</u>	<u>D. C. Amps.</u>	<u><math>R = \frac{E}{I}</math></u>
Off	4.5	0.35	12.9 $\Omega$
On	3.7	1.0	3.7
Off	6.3	1.90	3.3
On	6.0	2.0	3.0
Off	7.5	2.90	2.6
On	7.3	3.0	2.4
Off	8.6	3.95	2.2
On	8.5	4.0	2.1

(1) A. C. approximately 1 ampere

It is to be noted that at each level of direct current superimposition of alternating current resulted in a greater flow of direct current at a lower voltage, i. e., the apparent resistance of the cell was lowered. Furthermore, the quite reasonable finding was made that the effect was greatest when the A. C. and D. C. amperages were of the same order of magnitude and became almost negligible when the D. C. was about four times the A. C. These findings suggest that it might be worthwhile to carry through to completion an electrolysis using a platinum anode with superimposed A. C. on D. C. of comparable magnitudes. It would be of interest to know if the current yield held up. If so, it might be possible to improve substantially the power efficiency in present perchlorate production. Also, further experimentation would be required to determine if platinum loss remained the same or was altered by superimposed A. C.



At present we may only speculate upon the fundamental causes of the phenomena embodied in Table 6. One possibility is that the A. C. altered the chemical processes at the electrode and thence the electrode potential. A second possibility is that a rectification of the A. C. current occurred by virtue of the platinum anode. In any case, an interesting field of work is opened up by the findings.

#### Tantalum Strip Anode 123-53

As described elsewhere, Anode 123-53 failed in the standard process-test due to rapid polarization. This anode was of ductile tantalum 5.85 cm. long x 0.6 cm. wide x 0.038 cm. thick. After working the blue surface coating off the tantalum with emery paper, the strip was submerged to a depth of 3.85 cm. in the electrolytic bath.

When A. C. and D. C. sources were cut into circuit the D. C. ammeter (measuring flow from the storage battery) registered for a few seconds and then fell to zero. This may be interpreted as indicating polarization of the tantalum. When the D. C. power source was cut out of the circuit the D. C. voltmeter, measuring potential difference across the cell, fell to 1.6 volts, not to zero. This suggests that rectification of the A. C. was occurring. When the tantalum anode was removed from the bath it was found to be coated blue. When the blue coating was removed from the tantalum it was possible to repeat the experiment.

Thus, the hope that the surface of anodized tantalum would be altered by superimposition of 60 cycle A. C. so that perchlorate production could proceed was not realized.

#### Molybdenum Silicide Anode 123-49b

As described elsewhere, this anode became polarized in the regular

process-test. It was selected for superimposition of 60 cycle A. C. It was considered that such treatment might eliminate the polarization without affecting the oxidation resistance of the electrode.

In order to improve electrical contact the top of the anode was smoothed down by use of emery paper; a platinum lead-in wire was affixed. 3.9 cm. of the 7.2 cm. length was immersed in electrolyte. Electrolysis was started at a level of 0.4 amps. x 4.5 volts D. C. and dropped to a level of 0.2 amps. x 5.6 volts within nine minutes. It was then raised to a level of 3.0 amps. x 22.5 volts, which held for about eight minutes when the bath started to sputter. The anode was removed and examined.

It was found that the bottom 2 cm. of the electrode were badly attacked. Nascent chlorine could be smelled above the bath and a flocculent white precipitate was dispersed throughout the electrolyte. Salt had exuded out of the anode above the liquid level, presumably as a result of capillary action.

Apparently, in this case, superimposition was effective in destroying polarization. However, the depolarized anode did not have the ability to resist the oxidative attack of the bath.

#### Preliminary Experiments with 500 Cycle A. C. and Other Frequencies

##### Major Pieces of Equipment

Oscillator: Audio Oscillator. Hewlett-Packard. Model 200C. Amplifier: Bogen. Model H. E. 10. Voltmeter: Electronic Voltmeter. Ballantine Model 300.

##### Hookup and Operation

The amplified output of the audio-frequency oscillator was impressed on the cell circuit so that it passed through the cell and a length of manganin wire of exactly known resistance. The electronic voltmeter was

used to measure the voltage drop across the cell or the drop across the manganin wire. The magnitude of the current was computed from the latter measurement.

#### Platinum Anode

A platinum leaf anode (approximate dimensions 1.3 cm. x 0.3 cm) was selected for preliminary tests. D. C. electrolysis was started at the level of 1.3 amps. x 5.8 volts. 500 cycle A. C. to the extent of 1 amp x 1.4 volts was superimposed on the D. C. No effect of the A. C. superimposition on the D. C. meter readings was observed.

The oscillator frequency output was changed to 60 cycles per second. D. C. electrolysis was set to 1.2 amps. x 6.5 volts. When A. C. to the level of 1.6 amps. x 1.65 volts was introduced, the D. C. electrolysis level increased to 1.3 amps x 6.2 volts. Increase of A. C. to 8.6 amps. x 2.0 volts resulted in an increase in the D. C. electrolysis level to 1.35 amps. x 6.0 volts. When the A. C. was turned off the D. C. level dropped to 1.2 amps. x 6.5 volts.

At 20 cycles per second superimposed A. C. to the extent of 5.0 amps. x 1.25 volts enabled D. C. electrolysis at 1.3 amps. x 6.2 volts to occur. Without the A. C., the D. C. level was 1.25 amps. x 6.4 volts.

With 250 cycle superimposed A. C. to the extent of 12.8 amps. x 2.1 volts D. C. electrolysis occurred at 1.3 amps. x 6.0 volts. Without the A. C. electrolysis fell to 1.25 amps. x 6.3 volts.

#### Discussion of Results

A circuit for A. C. superimposition was assembled and found to function satisfactorily. Tests with a platinum anode indicated that the A. C. superimposition appeared to decrease the apparent resistance of the

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D. C. system at most frequencies tried. The experiments performed were only exploratory and will serve as the basis for further work.

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VII. Surface Oxidized Steels As Anodes

Many procedures exist for "blueing" or "blackening" steel to provide corrosion resistance. The blue or black films or coatings presumably consist of iron oxides. Magnetite may be the oxide in some cases. As the latter in bulk form is one of the promising perchlorate-anode materials the possibility exists that a magnetite coating would protect a steel substrate in the perchlorate process. Experiments were carried out to investigate this possibility.

123-57a, b, c. Molten  $\text{NaNO}_3$  -  $\text{KNO}_3$  Treatments

Three 3" lengths of 1/2" diameter cold rolled steel rod were selected. One was set aside untreated as a control. A mixture of 50 g.  $\text{KNO}_3$ , 50 g.  $\text{NaNO}_3$ , and 2 g.  $\text{MnO}_2$  was prepared by grinding the ingredients first separately and then together in a glass mortar. A 75 cc pyrex test tube was partly filled with this mixture and the tube and contents heated to about 320°C under which condition the salt mixture was molten.

Bar 123-57a supported by a copper wire was held below the surface of the molten salt for about 5 minutes. The treated bar was plunged in cold water, boiling water, and then hot oil. It was freed of most of the oil by wiping.

Bar 123-57b was first worked with emery paper to smooth the surface and then dipped in oil. After this the treatment was identical with 123-57a.

Bar 123-57c was the untreated control.

Bar 123-57a was completely immersed in the electrolyte solution. Electrolysis was started at 0.6 amps. x 2.8 volts and was discontinued after 5.8 amp.-hrs. The anode originally weighed 76.13 g. and lost

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0.08 g. in the process. A small amount of corrosion occurred above the platinum lead-in connection. The anode was blue-black below the platinum connection after electrolysis. The bath contained suspended solid particles.

Bar 123-57b was immersed to the extent of 4.0 cm. in the electrolyte solution. Electrolysis was started at 0.7 amps. x 2.9 volts and discontinued after 7.3 amp.-hrs. at 1.8 amps. x 3.6 volts. The electrode of initial weight 75.874 g. diminished by 0.146 g. The portion above the liquid level was badly scaled with a red-brown rust; the portion below the liquid level became blue-black in color. The bath contained suspended solid particles.

Bar 123-57c was immersed to a depth of 5.2 cm. in the electrolyte bath. Electrolysis was begun at a level of 1.9 amps. x 3.5 volts and continued for 7.2 amp.-hrs. to a level of 1.8 amps. x 3.8 volts. The anode of initial weight 75.785 g. lost 0.153 g. The portion of anode above the liquid level became badly scaled with a red brown rust. The portion below was blue-black in color. The bath contained suspended solid particles.

154-7a, b, c, d. Aqueous Nitrate Treatments

Cold rolled steel rods 1/4" diameter x 3" long were selected, carefully scrubbed with hot soapy water, immersed in toluene and set aside to air dry. A blackening solution was prepared by dissolving 80 g. NaOH, 2 g. KNO<sub>3</sub> and 2 g. NaNO<sub>3</sub> in 120 cc of distilled water. 154-7a was retained untreated as a control. 154-7b was immersed in the above solution for 15 minutes at 120°C, rinsed with boiling distilled water, dried and immersed in hot oil at 225°C for 10 minutes. 154-7c was immersed in solution for 20 minutes at 125°C, rinsed in hot distilled water, dried and immersed

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in hot oil for 10 minutes at 230°C. 154-7d was immersed in the solution for 30 minutes at 130°C, rinsed in hot water, dried, and immersed in hot oil at 225°C for 10 minutes.

The three treated bars acquired a black glossy sheen. The coatings appeared to be smooth and continuous. There were no apparent differences among the three treated bars.

154-7a. This anode, 7.7 cm. long x 0.63 cm. diameter, was completely immersed in the electrolyte bath. Electrolysis was begun at 2 amps. x 4.5 volts and continued for 2.3 amps.-hrs. to zero amperes. The anode initially weighed 18.767 g. and lost 3.616 g. Inspection showed that the anode had turned black during the process. Severe corrosion involving pitting occurred. The bath was turbid with red-brown rust particles which settled on standing. A small amount of black sediment was also present.

154-7b. This anode, 7.71 cm. long x 0.63 cm. diameter, was completely immersed in the electrolytic bath. Electrolysis was begun at 2 amps. x 4.2 volts and continued for 18.2 amps.-hrs. to a level of 0 amps x 11.4 volts. The anode initially weighed 18.700 g. and suffered a loss of 0.098 g. during the process. The anode - Pt lead connection became poor due to extensive corrosion which occurred above the bath level and electrolysis was stopped because of low current flow. The bath was turbid with corrosion products which settled on standing. A small amount of black sediment was present.

154-7c. This anode, 7.7 cm. long x 0.63 cm. diameter, was completely immersed in the electrolytic bath. Electrolysis, begun at 2 amps. x 4.7 volts, was continued for 22.2 amp.-hrs. to a level of 1.8 amps. x 5 volts. The anode which initially weighed 18.725 g. lost 2.450 g. The

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anode was badly pitted and covered with corrosion products. The bath contained a lot of corrosion products and some black sediment.

154-7d. This anode, 7.7 cm. long x 0.63 cm. diameter, was completely immersed in the electrolytic bath. Electrolysis was begun at a level of 2 amps. x 4.9 volts and continues for 25.4 amp.-hrs. to a level of 1.2 amps x 8 volts. The anode which initially weighed 18.716 g. suffered a loss of 2.762 g. The anode was covered with much corrosion products. When this was removed by washing it was noted that the anode was badly pitted. The bath contained much corrosion product and some black sediment.

154-11-1, -2, -3, -4. Sodium Nitrite Treatments

Four bars of cold rolled mild steel of cross-section 0.63 cm. x 0.63 cm. and lengths as indicated individually for each specimen below were cut and polished on a sander to remove dirt and rust spots. The polished samples were washed in a solution of Alconox detergent, rinsed with hot water, then acetone, and dried. 154-11-4 was set aside untreated, as a control. 154-11-1 was dipped in molten sodium nitrite contained in a zircon crucible. The initial temperature of the salt was 420°C and it fell and was maintained between 340-360°C during the dipping. The specimen was kept in the salt bath for 15 minutes, removed, rinsed with hot water and placed in a hot oil bath for 5 minutes at 180°C. 154-11-3 was held in the molten salt for 20 minutes at 400°C. It was rinsed with hot water, dried, acetone rinsed, dried, and placed in a hot oil bath at 210°C for 5 minutes. 154-11-2 was held in the molten salt bath at 420°C for 30 minutes. It was rinsed with hot water, dried, acetone rinsed, dried and placed in a hot oil bath at 220°C for 5 minutes.



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154-11-4. Resistance of this anode was 6.0 milli ohms. It was 3.47 cm. long and completely immersed in the electrolytic bath. Electrolysis was started at a level of 1.55 amps. x 4.8 volts and continued for 15.9 amp.-hrs. (13 hours) to a level of 1.1 amps. x 7 volts. The anode which weighed 11.217 grams initially decreased in weight 5.855 g. Inspection showed the anode to be corroded with some portions black and others rust colored. The anode had dissolved away under the bath level to the shape of an inverted pyramid. The bath contained a lot of solid corrosion products and was quite viscous.

154-11-1. Resistance of this anode was 40 milli-ohms. It was 3.99 cm. long and completely immersed in the electrolytic bath. Electrolysis was started at a level of 2 amps. x 3.7 volts and continued for 20.4 amp.-hours (13 hours) to a level of 1.6 amps. x 5.8 volts. The initial weight of the anode was 12.027 g.; it was so seriously corroded that a final weight was not taken. Of the lower 2 cm. only a needle-like rod remained. The bath was quite viscous due to solid corrosion products.

154-11-3. Resistance of this anode was 22 milli-ohms. It was 3.84 cm. long and completely immersed in the electrolytic bath. Electrolysis was begun at 1.6 amps. x 4.8 volts and continued for 8.8 amp.-hrs. (6.5 hours) to a level of 1.3 amps. x 6 volts. The anode initially weighed 11.578 g. and suffered a loss in weight of 4.112 g. Inspection showed the anode to be covered with rust and disintegration had occurred forming triangular faces on the sides of the bar. The bath was viscous with solid corrosion products.

154-11-2. The resistance of this anode was 61 milli-ohms. It was 3.8 cm. long and completely immersed in the electrolytic bath. Electrolysis was started at 1.7 amps. x 4.0 volts and continued for 4.9 amp.-hrs. (3 hrs.

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20 min.) to a level of 1.5 amps. x 6.8 volts. The anode weighed 11.460 g. initially and lost 6.534 g. The anode was coated with corrosion products and had partially disintegrated. The bath was viscous. Sputtering and fuming were observed towards the end of the electrolysis and the process was discontinued on that account.

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VIII. Some Theoretical Considerations\*

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1. Protective Film Theory of Oxidation Resistance

Dr. Searcy favors the view that high temperature oxidation resistance of molybdenum disilicide is due to the existence of a protective layer, probably silicon dioxide, on the surface of the massive material (substrate). Without such an hypothesis it is difficult to explain how the molybdenum and silicon could remain in the lower oxidation state which occurs in  $\text{MoSi}_2$ . Accepting the "protective film" theory, a number of deductions can be made that might prove useful in guiding experiment.

One criterion, that has been long suggested, for a film to "protect" its "substrate" is that the molar volume of the substance in the film be greater than the molar volume of the substrate material. This principle is said to have some experimental confirmation. In any case, the necessary calculations based on the density of the materials in film and substrate may be made and the results compared with experiment or used to suggest experiment. Dr. Searcy said that, on the molar volume basis, the other silicides of molybdenum should prove to have less effective oxidation resistance than  $\text{MoSi}_2$ .

In addition to meeting the molar volume criterion a film should be "self-healing". If broken, it must be possible for substances in the environment to react with the exposed substrate in such a way as to reform the film. If this is not possible, serious corrosion may occur.

A fundamentally important parameter is the free energy of formation

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\* On June 2, 1953 the writer conferred with Dr. Alan W. Searcy of Purdue University. The content of the present section is, essentially, the ground covered in that discussion. Of course, Dr. Searcy cannot be held responsible for the points presented here as he did not participate in writing the report.

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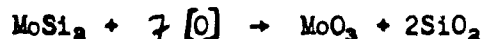
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of the compound comprising the surface film. Consistent with the highly electro-negative character of oxygen, the common oxides are generally quite stable compounds. As mentioned above, silica ( $\text{SiO}_2$ ) is considered to be the protective material giving molybdenum disilicide its high-temperature oxidation resistance.

## 2. Free Energy of Formation of Oxides and Film Stability

The relationship among the free energies of formation of the possible oxides that may form from elements in the substrate may also be critical for formation of a proper film. In the case of molybdenum disilicide, where both components are in a relatively low state of oxidation we might expect the formation of mixed oxides as follows:



Dr. Searcy suggests that since  $\text{MoO}_3$  is considerably less stable than  $\text{SiO}_2$ , it either does not form at all, or if formed, it reacts in the sense of the following equation.



$\text{Mo}_3\text{Si}_2$  is a phase in the Mo-Si system identified by Searcy.

Based on this consideration we would not expect  $\text{MoO}_3$  to form in a net reaction.

The application of a similar line of reasoning to the case of titanium disilicide does not result in the elimination of  $\text{TiO}_2$  as a possible film component. Since the stabilities of  $\text{TiO}_2$  and  $\text{SiO}_2$  are of the same order we would not expect  $\text{TiO}_2$  to be reduced by  $\text{TiSi}_2$  as with  $\text{MoO}_3$  and  $\text{MoSi}_2$ . Instead of a one-component film we would expect a two-component film of  $\text{TiO}_2$  and  $\text{SiO}_2$  which might offer less protection than a film of silica alone. It might be relevant in this connection to recall that titanium

metal is easily oxidized at high temperatures; the oxide does not afford protection.

### 3. Magnetite ( $\text{Fe}_3\text{O}_4$ ) Protected by $\text{Fe}_2\text{O}_3$

Magnetite exhibits oxidation resistance in spite of the fact that the iron present is not in its highest oxidation state. Dr. Searcy suggests that it would be of interest to examine titanium and vanadium analogues of magnetite to see if the same type of protective film occurs.

### 4. Ceramic Coated Conductor

Dr. Searcy pointed out that the film theory of oxidation resistance suggests another general approach to chlorate-anode preparation. It might be possible to coat a relatively base metal with a properly chosen ceramic film. A sufficiently thin film, even though having high resistivity, will offer low resistance to the passage of the electric current.

It happens that Horizons had already been considering this approach. In fact, Mr. Fenity of the Ceramics Department had made some preliminary computations concerning film thicknesses, core thicknesses and over-all resistance of such anodes. Mr. Fenity indicated that in the ceramics field, relevant techniques are currently under active study.

For our application, silica and titania coating might prove feasible. We know that titania does not confer high temperature oxidation resistance on titanium. However, this does not mean that a substrate cannot be found which will be afforded protection by  $\text{TiO}_2$ .

### 5. Mechanism of Conduction Through the Film

During the course of the discussion it became evident to Dr. Searcy and the writer that the mechanism of electrical conduction through the

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protective film was another factor to be considered in the chlorate-anode problem. There are various bodies of work in the literature (semi-conduction, diffusion, tracer studies) which might fruitfully be consulted in this connection.

If we consider the oxide film which may be responsible for the relative stability of some substances to an oxidizing attack we may imagine the entities which carry electricity to be

- (a) Electrons
- (b) Positive ions
- (c) Negative ions (i. e. oxide)
- (d) Holes, positive or negative

A film which properly covers a substrate and which is thermodynamically stable may nonetheless suffer deterioration, for example, if oxide ions migrate through it and attack the substrate.

#### 6. Protective Films Other Than Oxides

Fluorine is more electronegative than oxygen and it is reasonable to consider that suitable fluoride protective films might be found. Chlorides do not prove as promising. We know that copper and nickel attain stability to further oxidizing attack by virtue of the formation of protective fluoride layers. The thermodynamic stability of fluorides is high compared to that of the corresponding oxides, i. e.,  $\text{CuF}_2$  and  $\text{CuO}$ . It might be of interest to compute the molar volumes of these substances.

#### 7. Resistance of Porous Bodies

Applying the film theory to porous bodies of, say, molybdenum disilicide we would expect the silica film to form throughout the "internal surface" of the anode as well as on the external surface. It is possible

that the oxidizing attack entailed in forming the silica would tend to reduce the metallic conducting paths from grain to grain of the substrate and thus increase total resistance.

#### 8. Quality of Oxide Films

Dr. Searcy made the point that the nature of the oxide film might be significantly different depending on whether the film were formed during the firing of the anode or during the electrolysis. For example, we might expect a relatively ineffective hydrated silica to form in the aqueous electrolytes medium while an anhydrous coherent film would form on high temperature oxidation.

It might be possible to control the quality of the film by selection of firing conditions.

We have been preparing molybdenum disilicide anodes either in an inert atmosphere or in vacuum. However, it is not impossible that enough oxygen has contaminated the systems to produce silica films. This could readily be tested by scraping a fresh surface on an anode in an inert atmosphere and comparing the behavior with that of a control anode during electrolysis.

#### 9. Firing the Silicides

In regard to the loss of silicon in heating molybdenum disilicide in vacuum, Dr. Searcy suggested that we could

- (a) Use an excess of silicon
- (b) Use an argon atmosphere

The writer pointed out that since our interest is in massive bodies rather than powder the use of excess silicon, while permitting production

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of the correct over-all stoichiometric proportions of the components, would not correct the non-homogeneous distribution of silicon from the center to the surface of the rod due to silicon diffusion.

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